

FIG. 1B

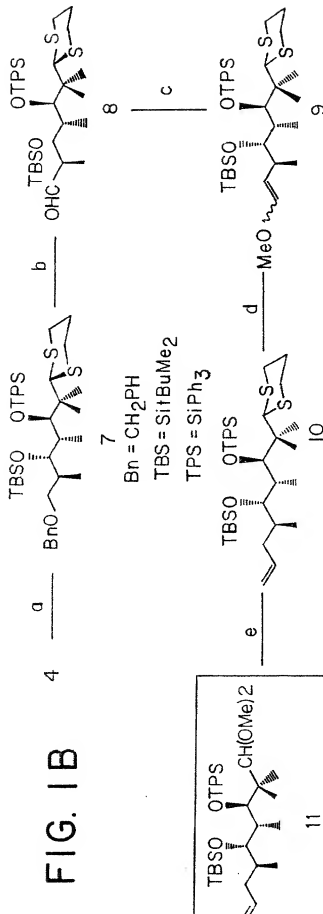


FIG. 12B

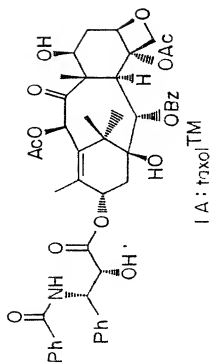
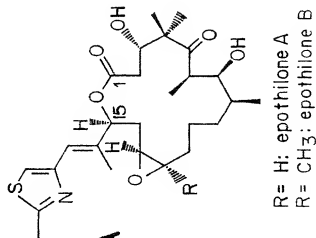
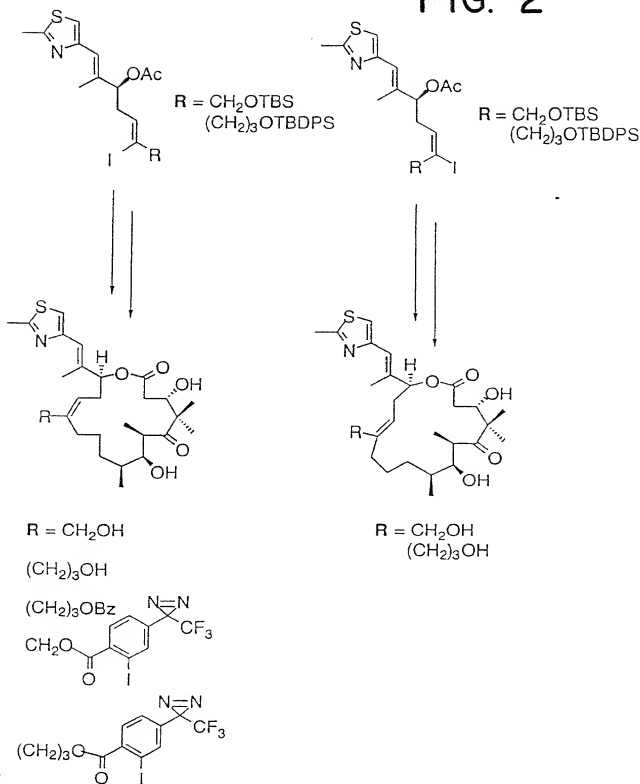


FIG. 12A



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FIG. 2



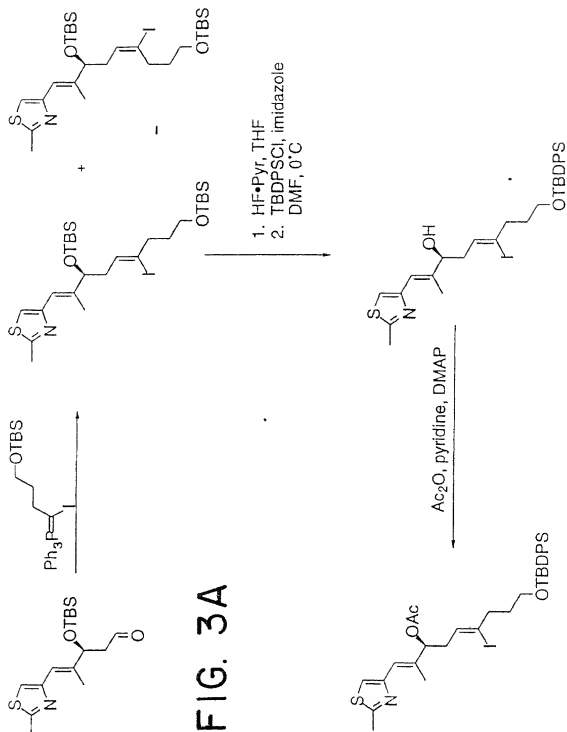


FIG. 3A

FIG. 3B

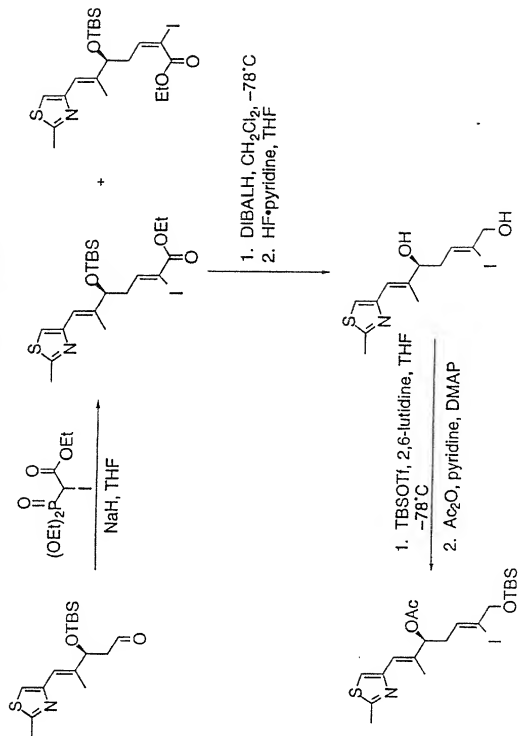
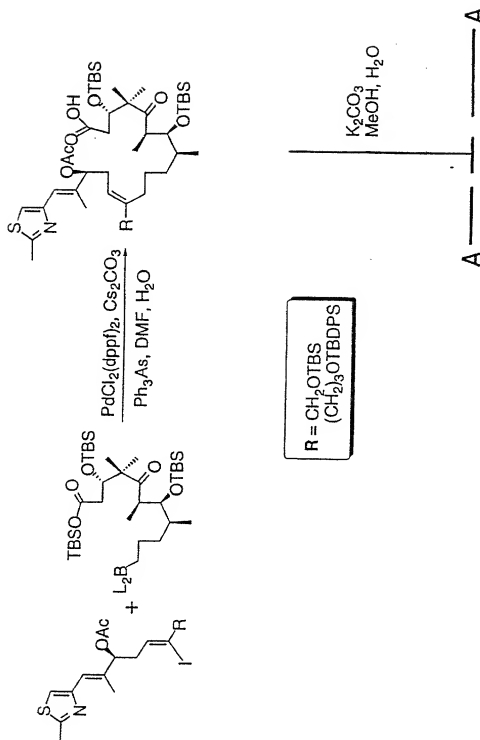


FIG. 3C



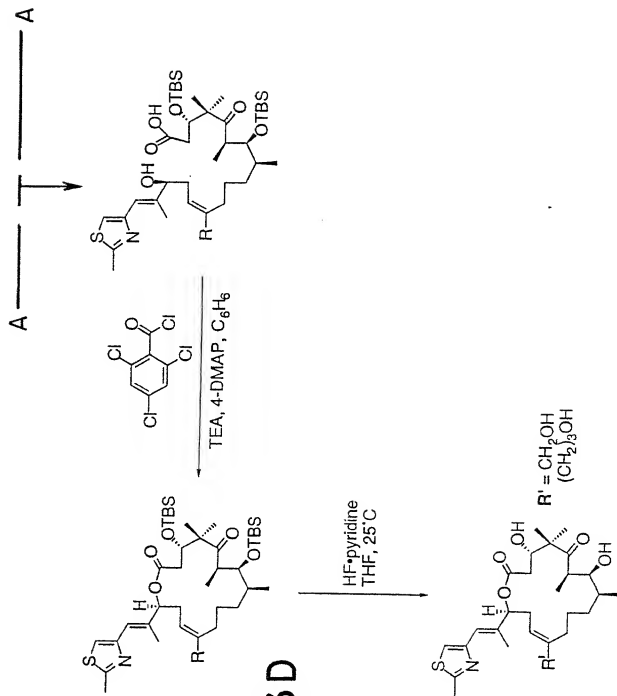


FIG. 3D

FIG. 3E

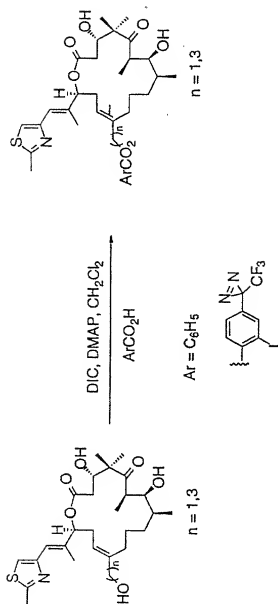


FIG. 3F

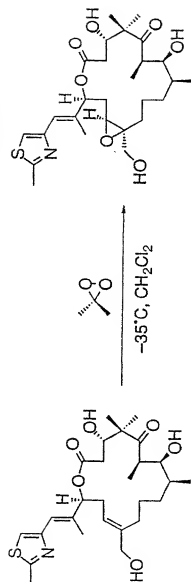


FIG. 4A

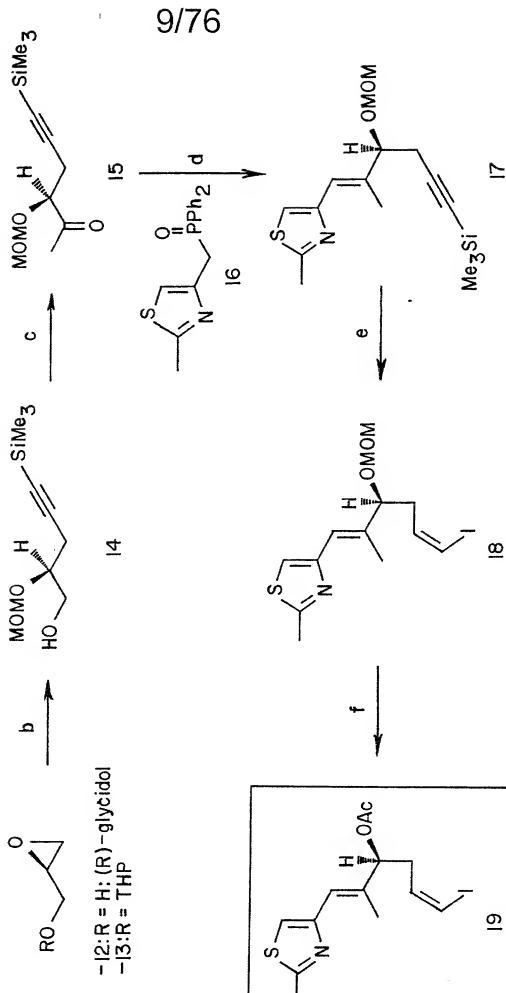
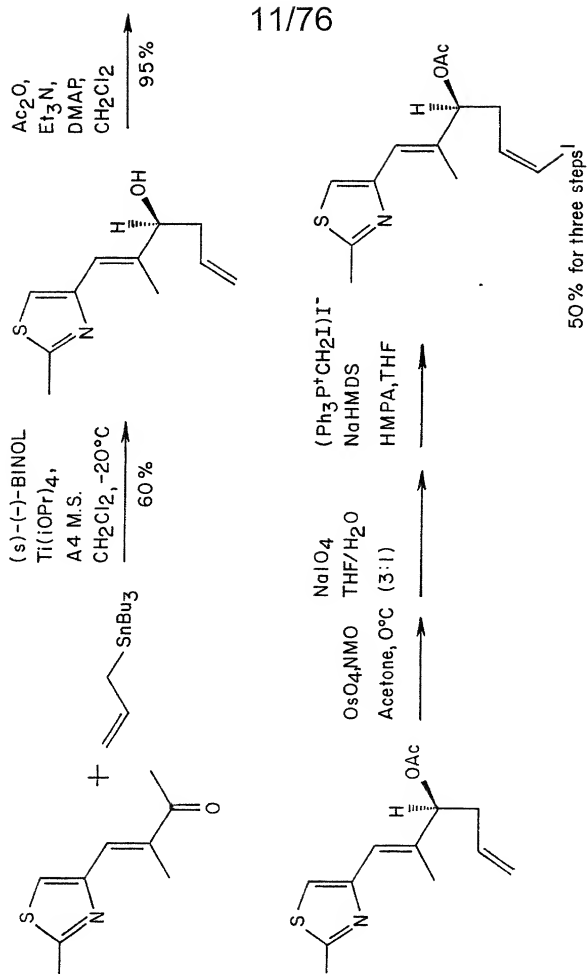


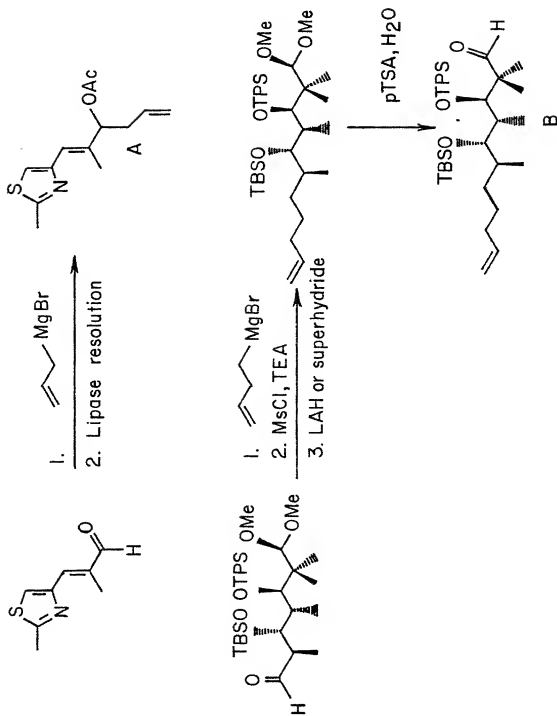
FIG. 5

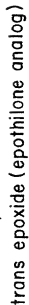


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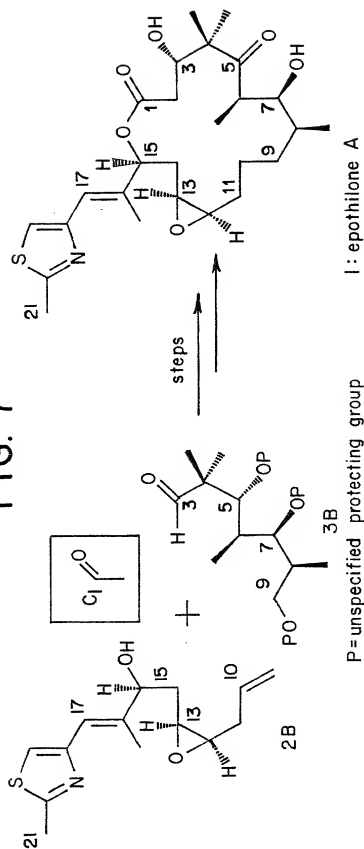
FIG. 6A





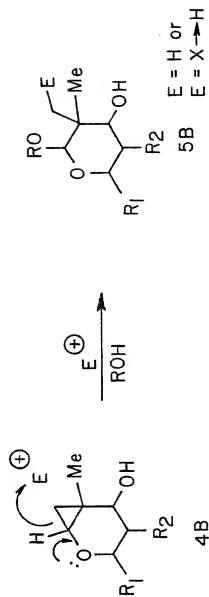
*17 steps from known starting materials vs. 27 steps for aldol macrocyclization

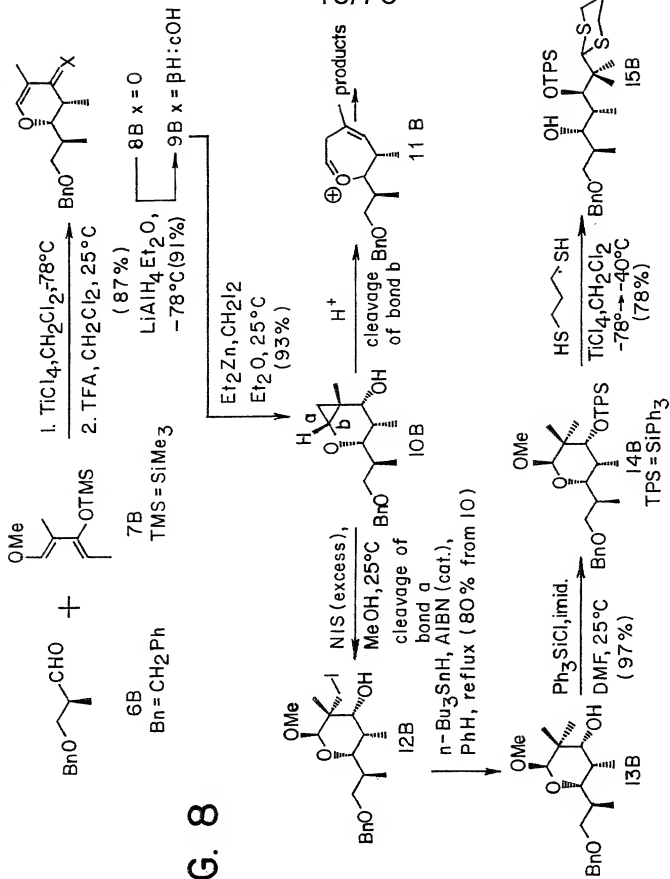
FIG. 7



P=unspecified protecting group

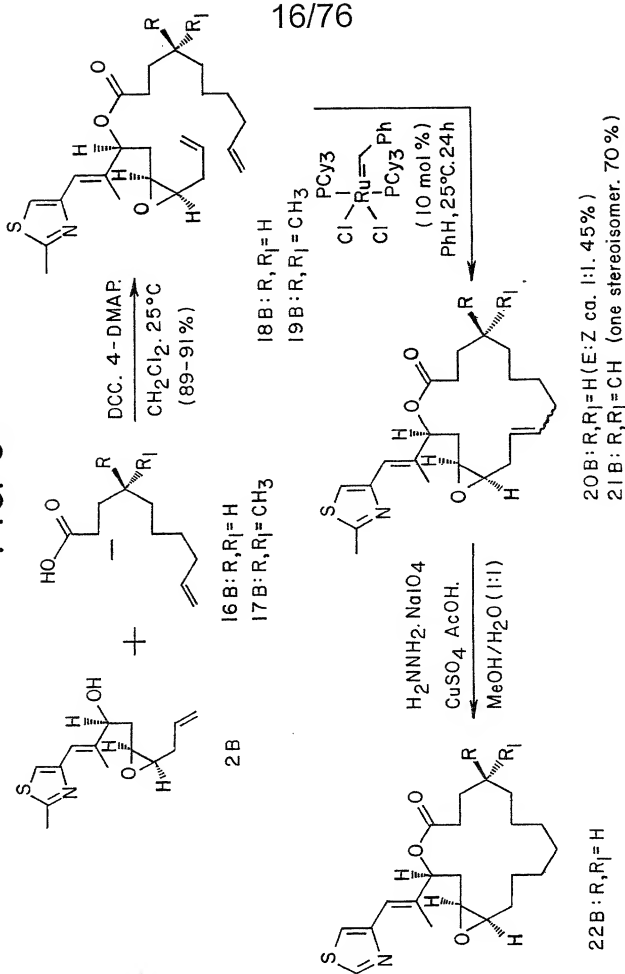
Convergent strategy for a total synthesis of epothilone A (1).





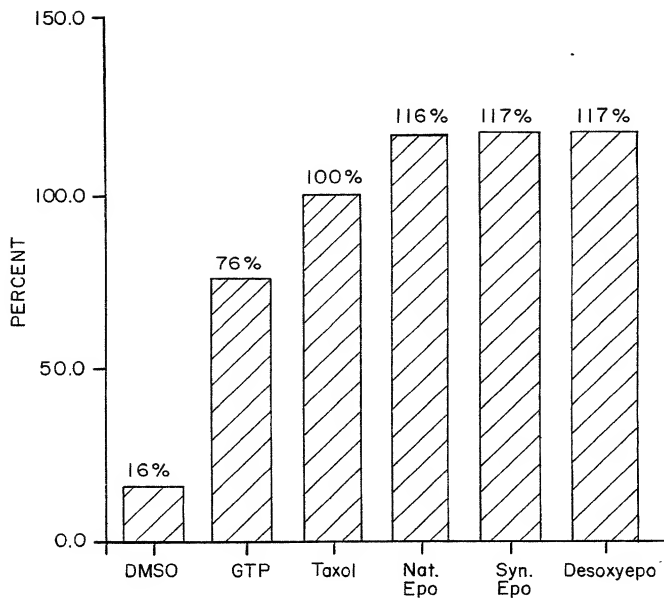
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FIG. 9



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FIG. 10



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FIG. 11

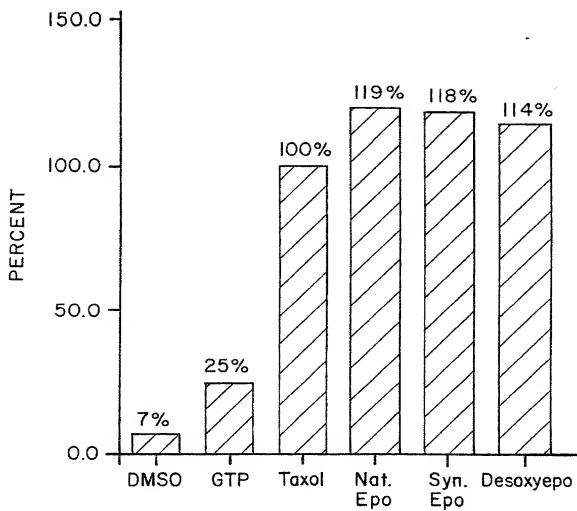


FIG. 13

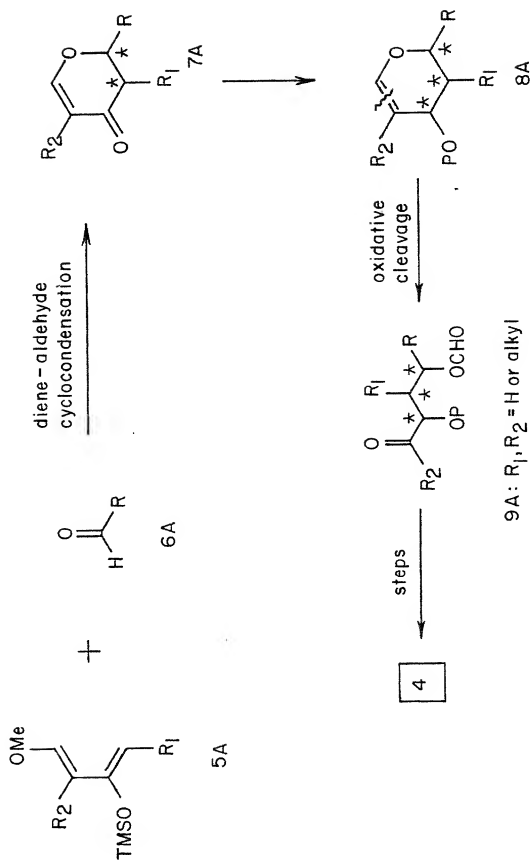


FIG. 14A

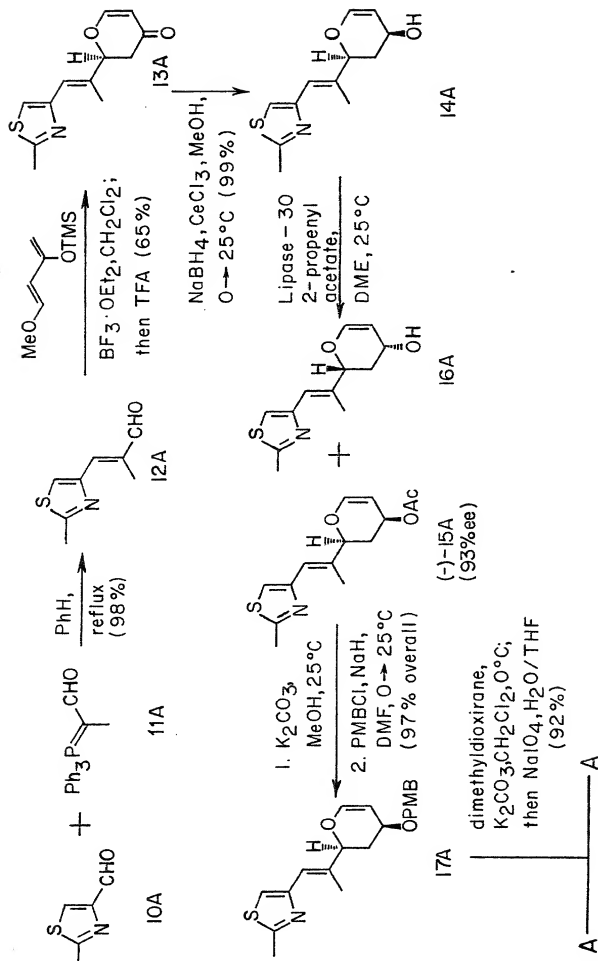
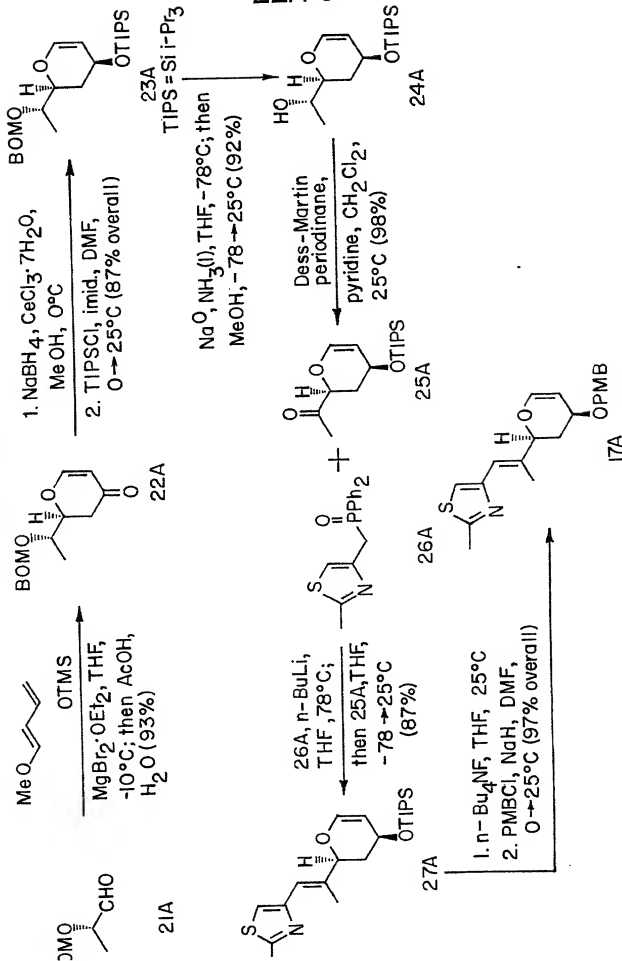


FIG. 15



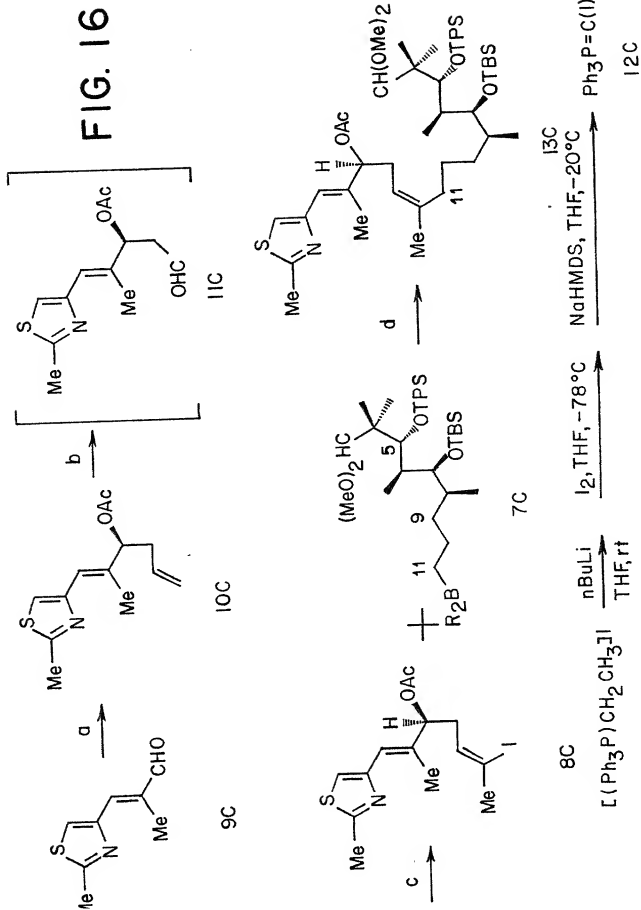
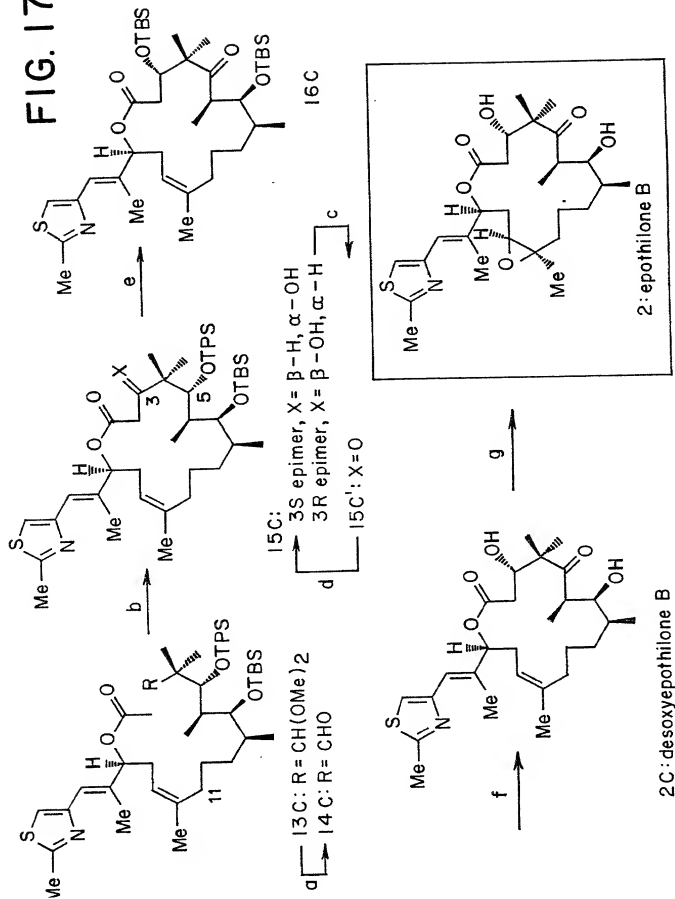


FIG. 17



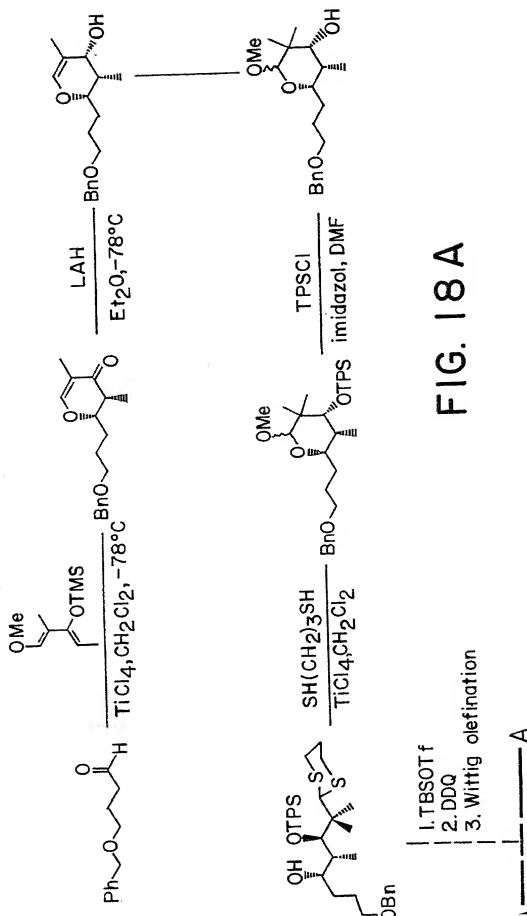


FIG. 18A

FIG. 18B

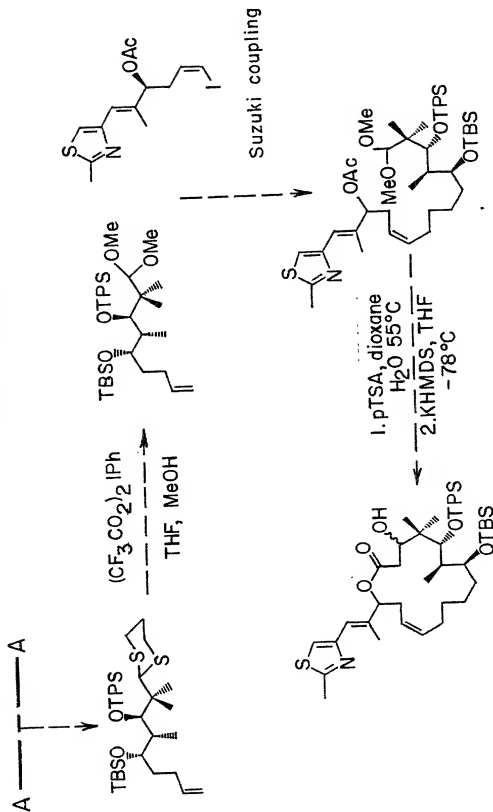


FIG. 19A

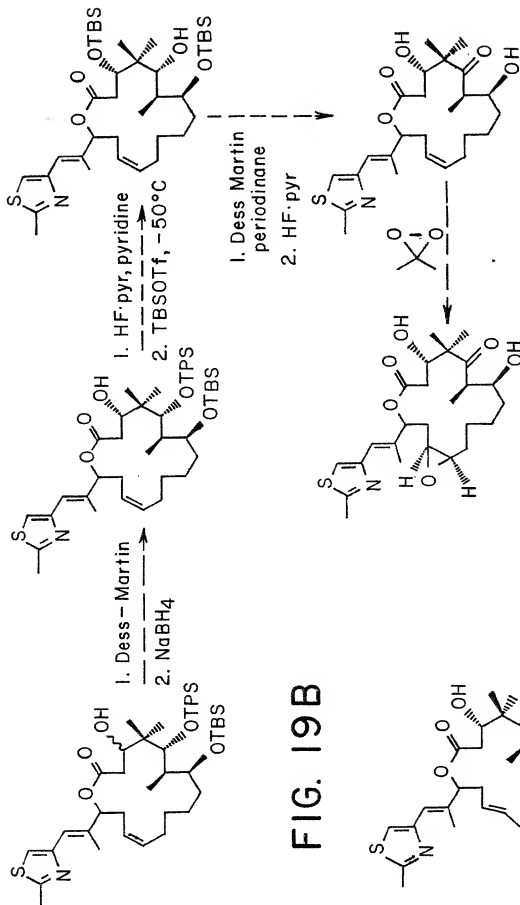
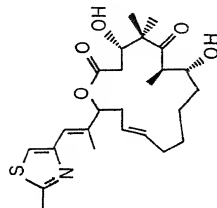


FIG. 19B



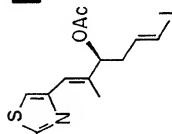


FIG. 19C

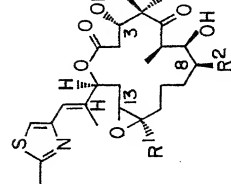
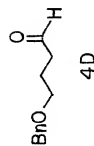


FIG. 20A

$R^1 = H, R^2 = \text{Me}$; epothilone A

$R^1 = R^2 = \text{Me}$; epothilone B

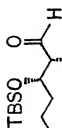
$R^1 = R^2 = H$; Cg-desmethyl-epothilone A (3D)



a, b



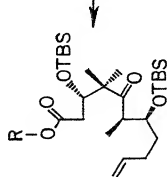
c



d

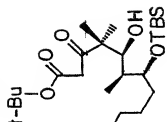
TBS = Sit-buMe₂

FIG. 20B



k

e, f



7D

8D

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FIG. 21

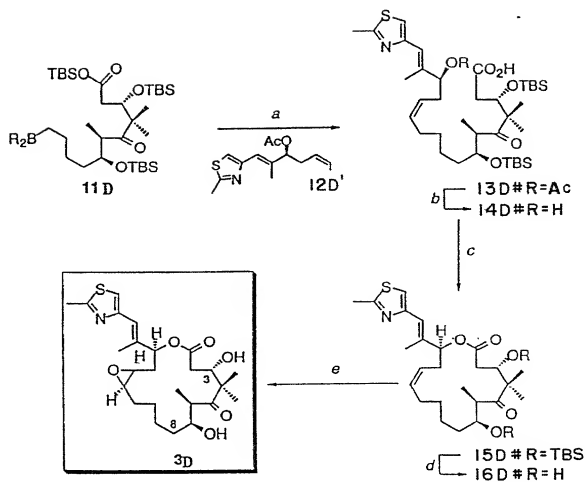


FIG. 22A

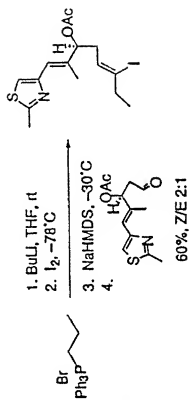


FIG. 22B

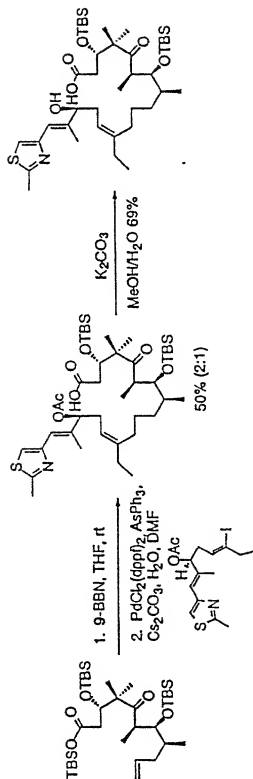


FIG. 22C

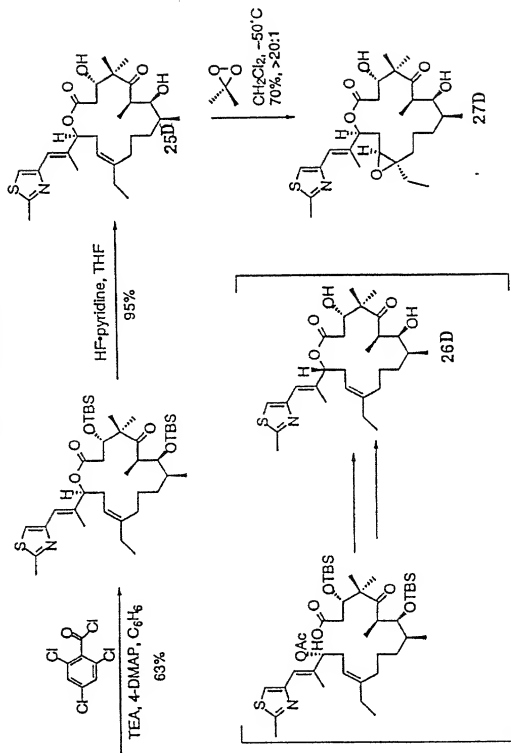


FIG. 23A

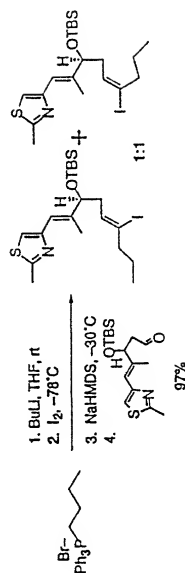


FIG. 23B

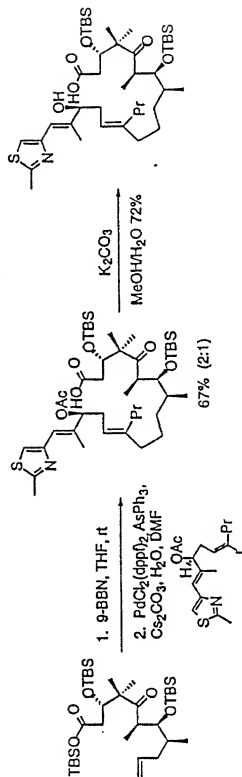


FIG. 23C

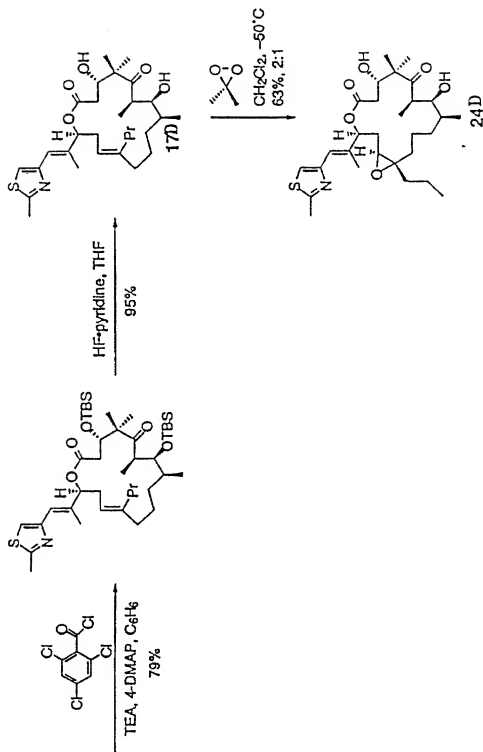


FIG. 24A

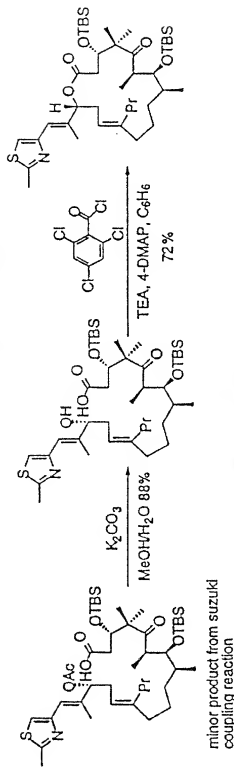


FIG. 24B

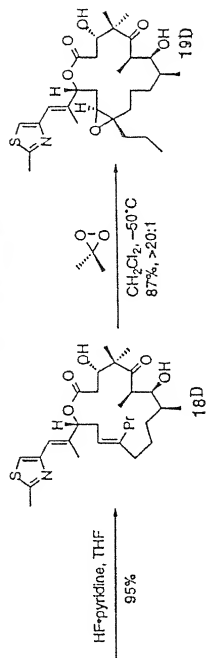


FIG. 25A

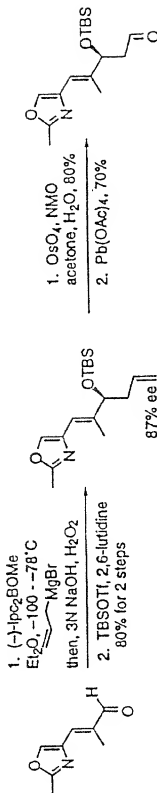


FIG. 25B

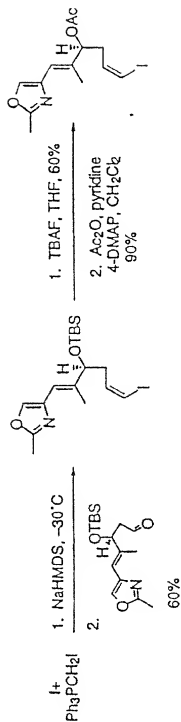


FIG. 25C

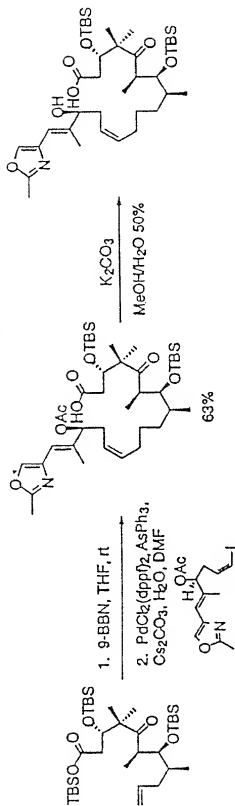


FIG. 25D

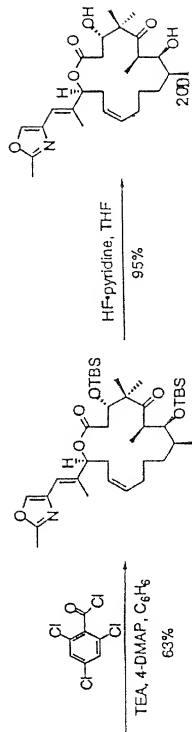


FIG. 26A

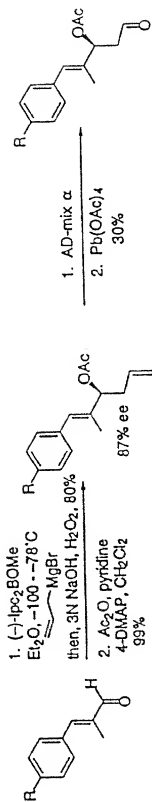
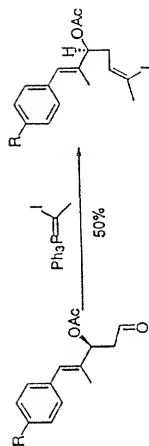


FIG. 26B



R = H, F, CF_3
 R=H is the only compound
 completed, F and CF_3 are nearly
 completed

FIG. 26C

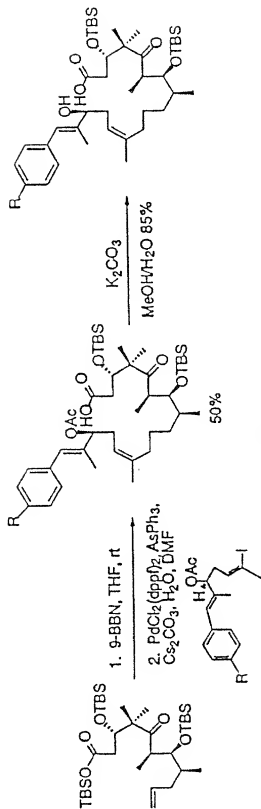


FIG. 26D

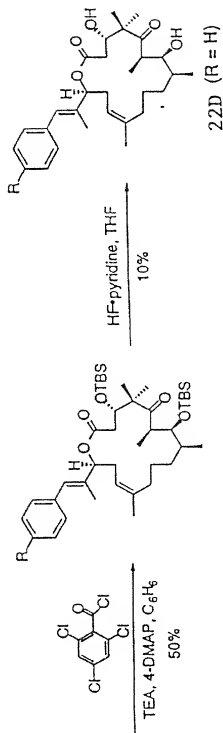


FIG. 27B

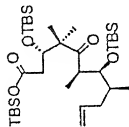
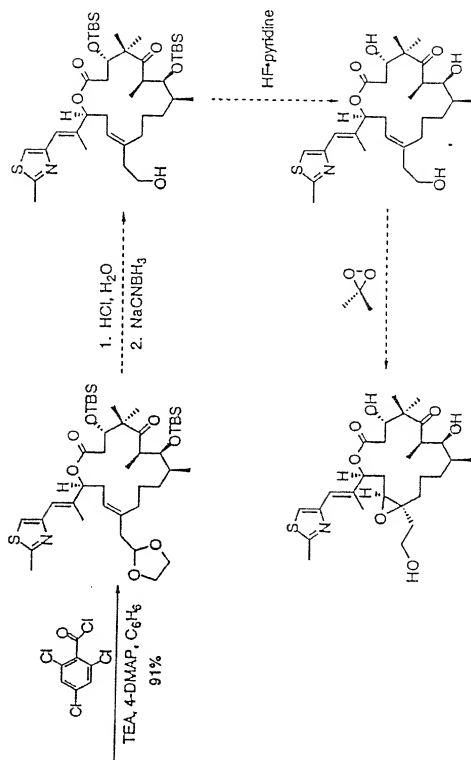
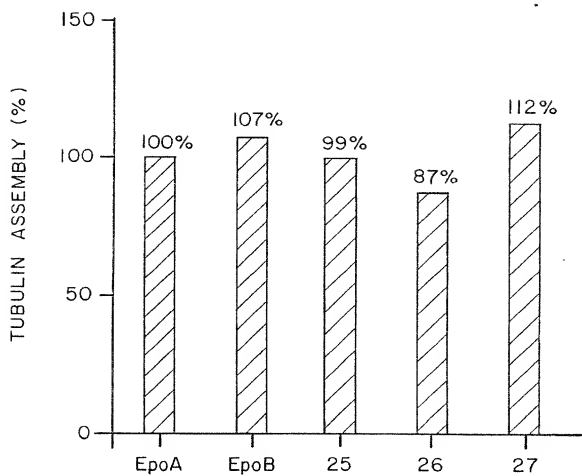


FIG. 27C



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FIG. 28A



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FIG. 28B

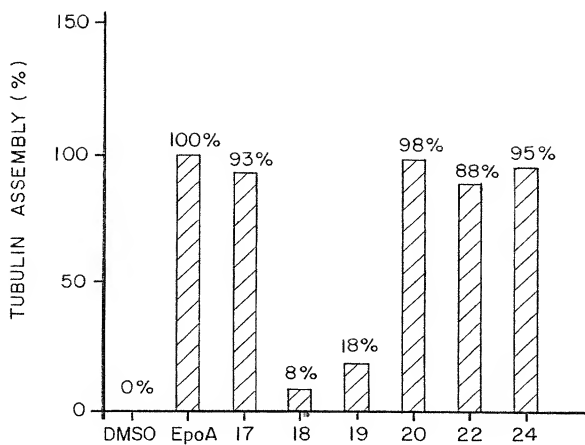


FIG. 29

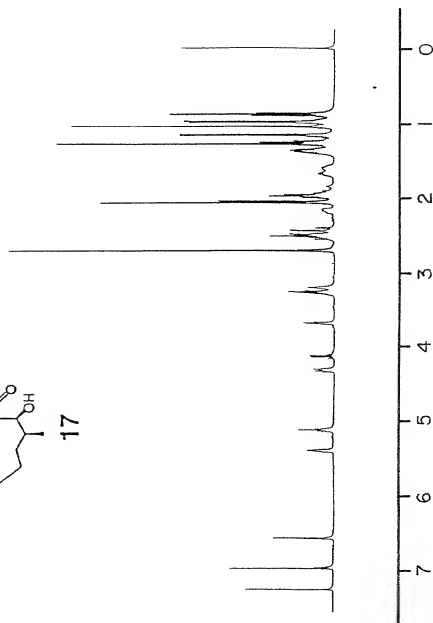
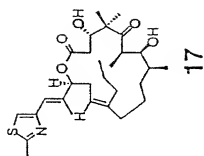
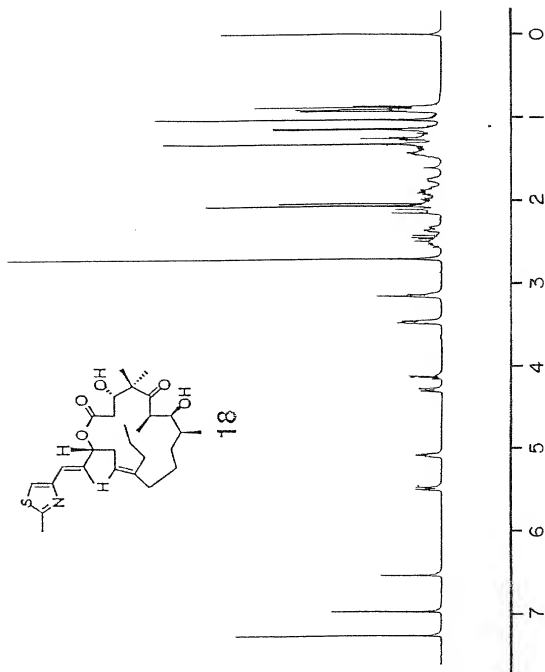
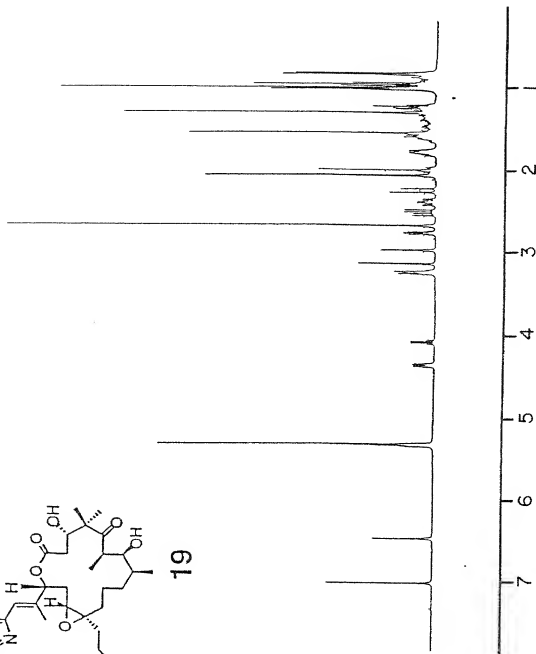
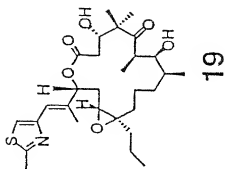


FIG. 30

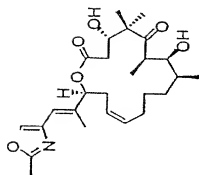


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FIG. 32



20

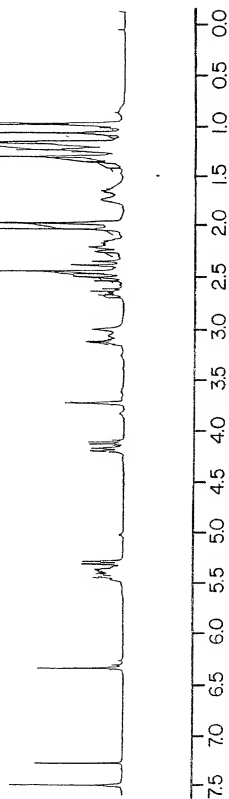
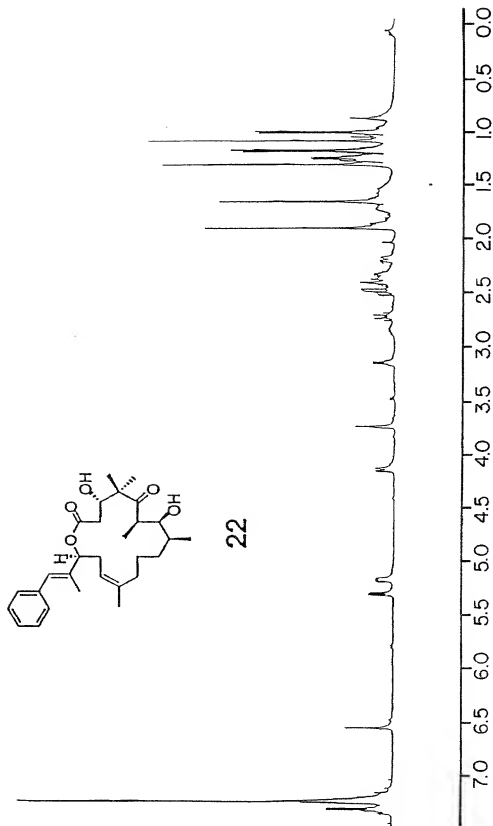
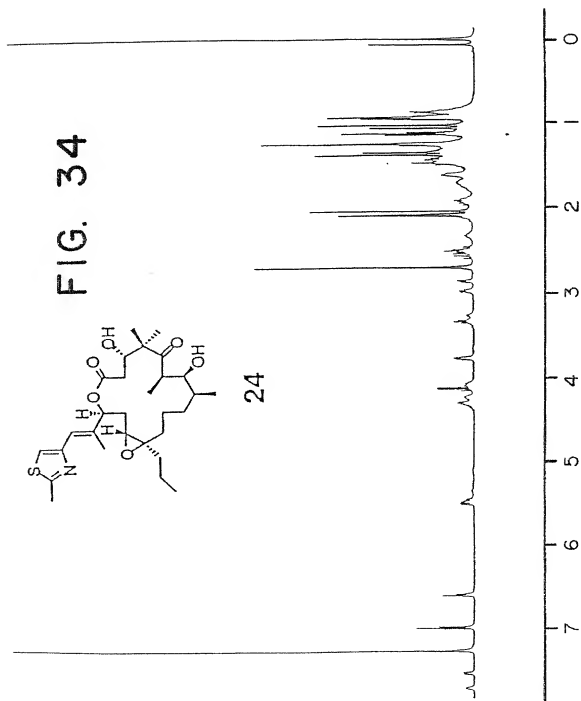
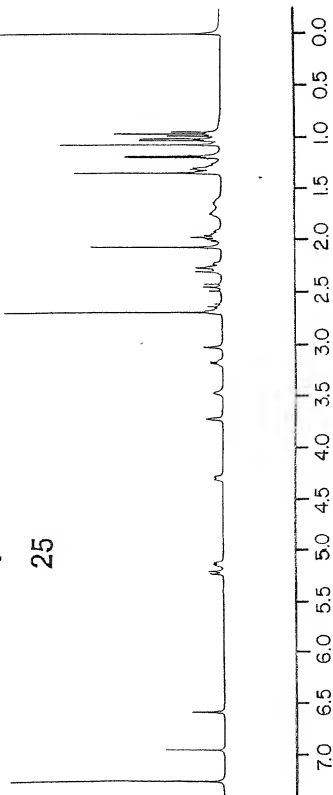
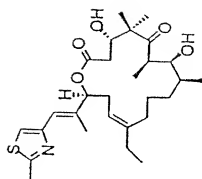


FIG. 33





25



26

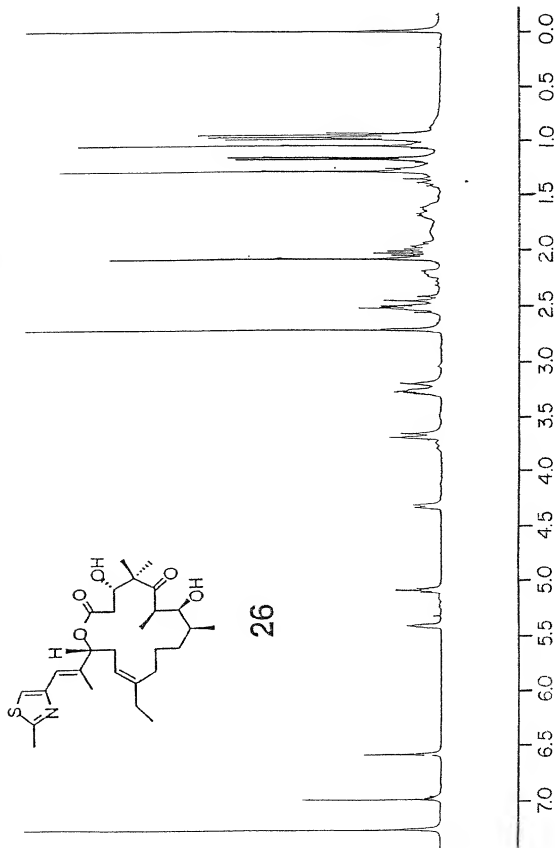


FIG. 37

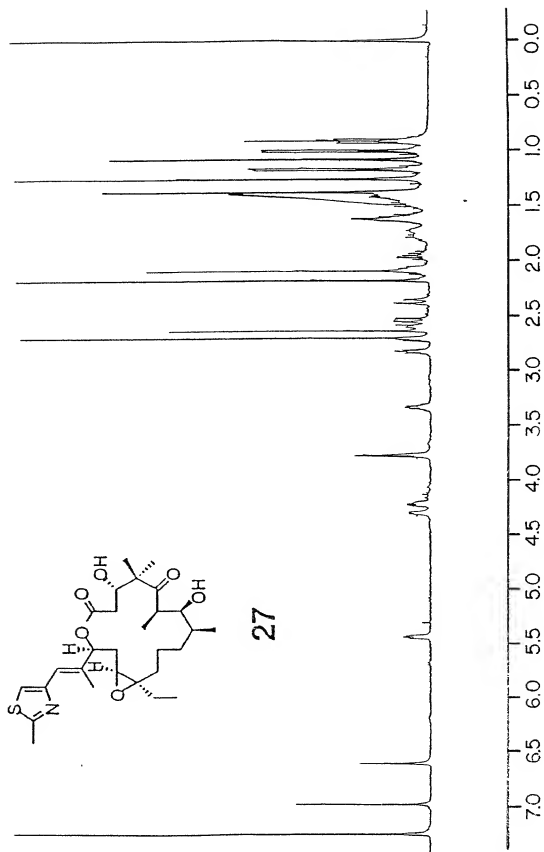


FIG. 38

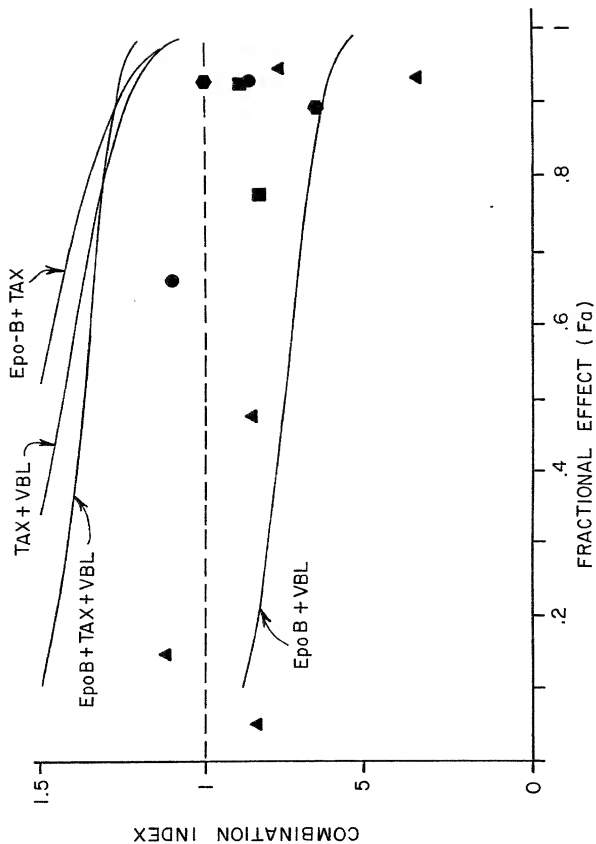
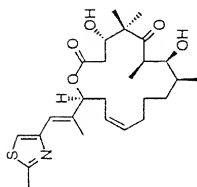
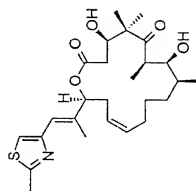


FIG. 39A

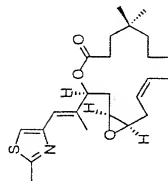


desoxyepothilone A

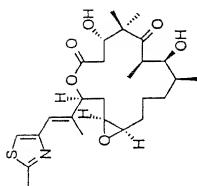
1

(0.022)
[0.012]

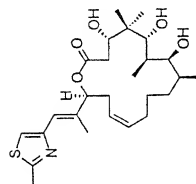
4

(2.12)
[43.0]

3

(271.1)
[22.4]

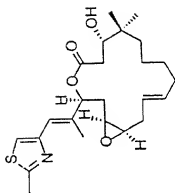
epothilone A

(0.0027)
[0.020]

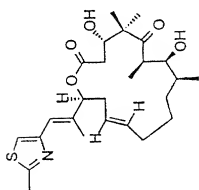
2

(14.23)
[6.28]

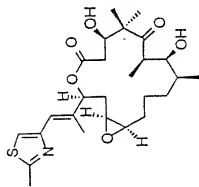
FIG. 39B



7
(7.36)
[9.82]

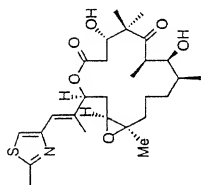


6
(0.052)
[0.035]

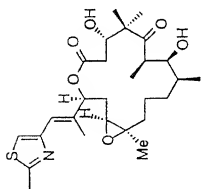


5
(>20)
[35.2]

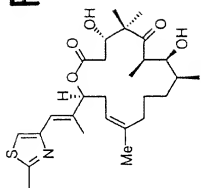
FIG. 40A



synthetic epothilone B

8(0.00044)
[0.0026]

natural epothilone B

9(0.00017)
[0.0012]

desoxyepothilone B

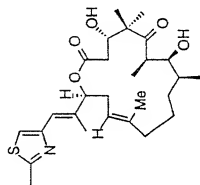
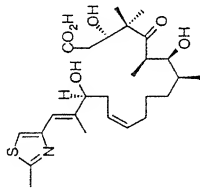
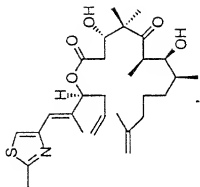
10(0.0095)
[0.017]**11**(0.090)
[0.262]**12**(0.79)
[>5]**13**(11.53)
[5.63]

FIG. 40B

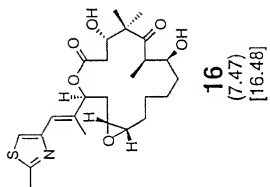
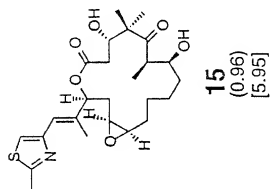
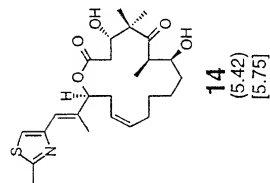
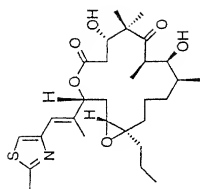
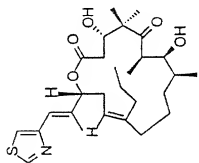


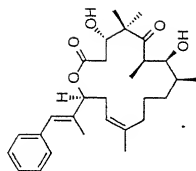
FIG. 41A



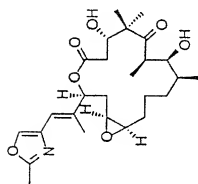
17
(0.090)
[0.254]



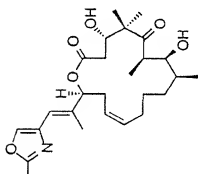
18
(1158)
[>720]



19
(0.96)
[>1.0]



20
(0.030)
[0.049]



21
(0.098)
[0.146]

22
(0.098)
[0.146]

FIG. 41B

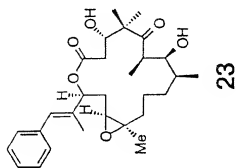
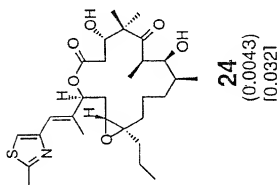
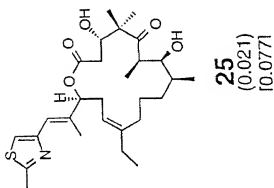
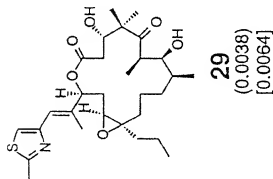
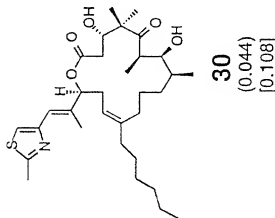
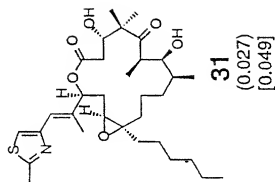
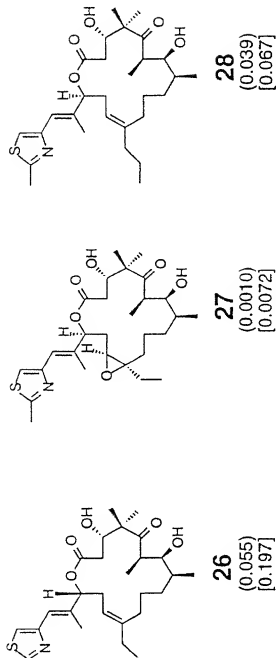


FIG. 42A



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FIG. 42 B

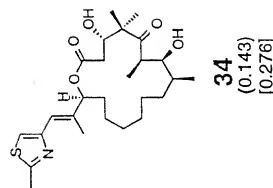
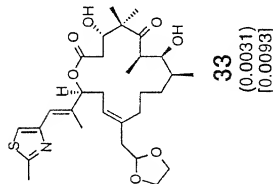
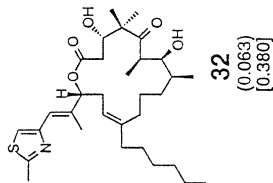
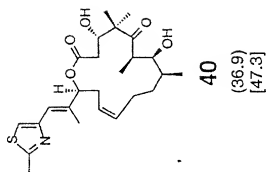
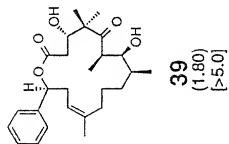
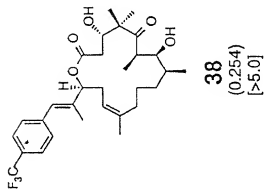
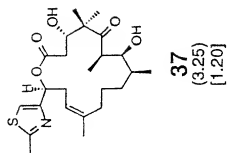
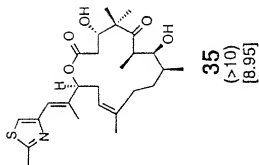


FIG. 42C



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FIG. 42D

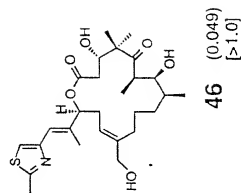
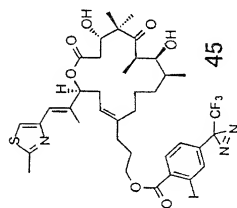
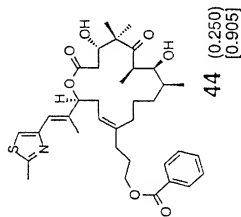
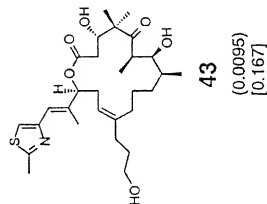
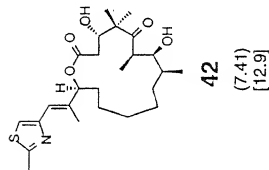
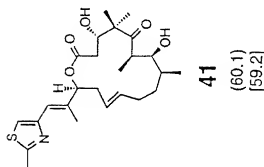
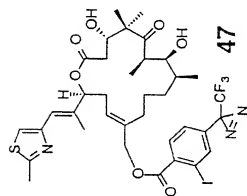
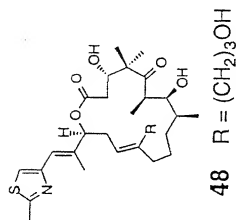
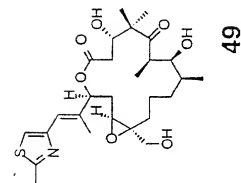
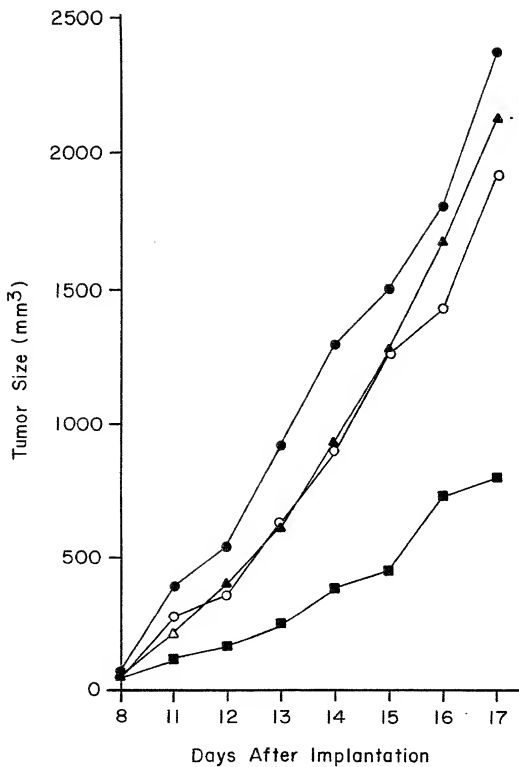


FIG. 42E



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FIG. 43A



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FIG. 43B

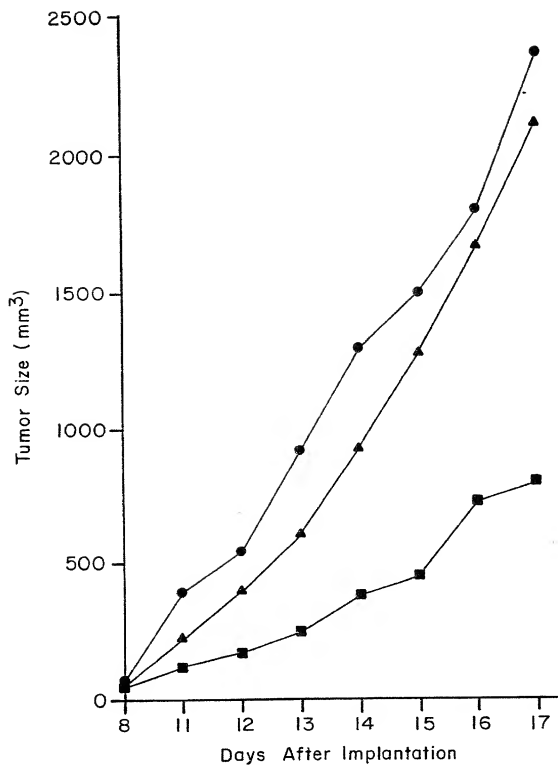


FIG. 44A

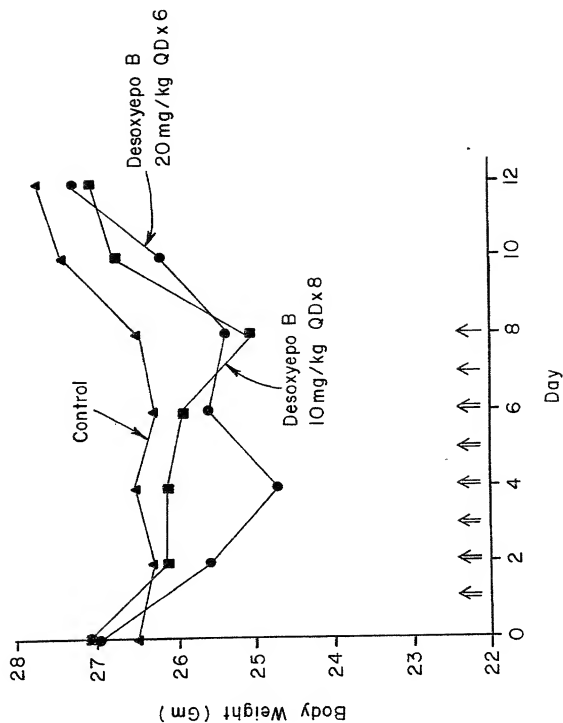
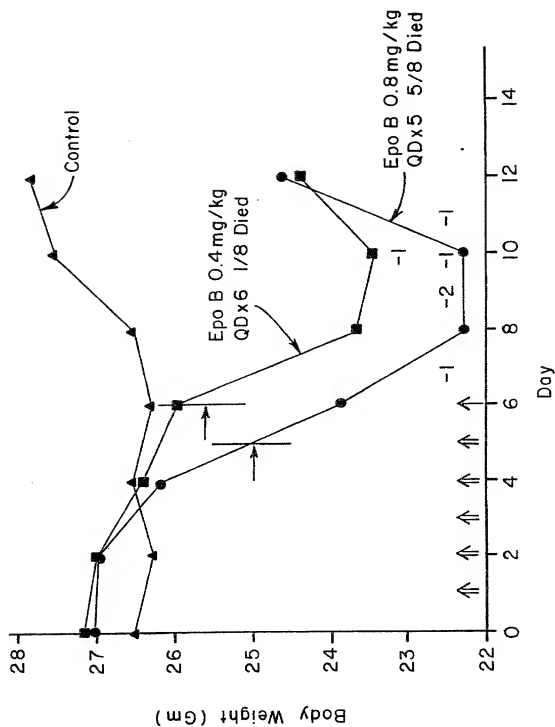
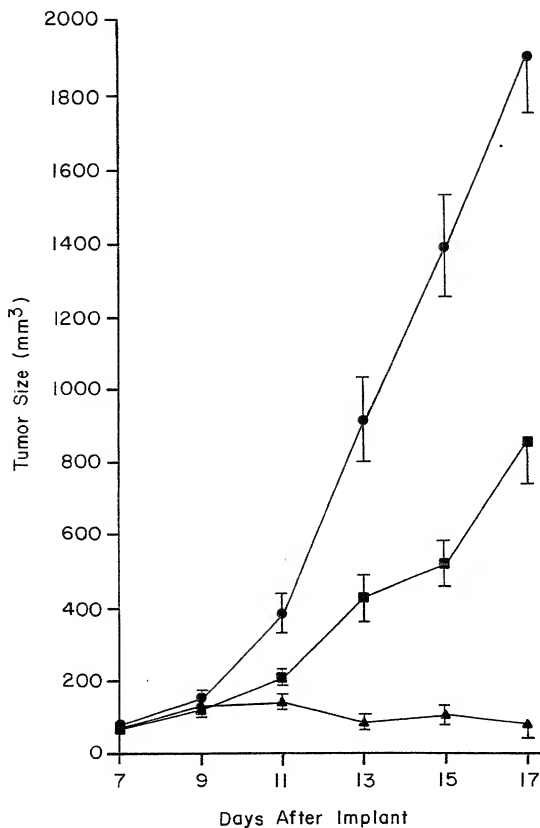


FIG. 44B



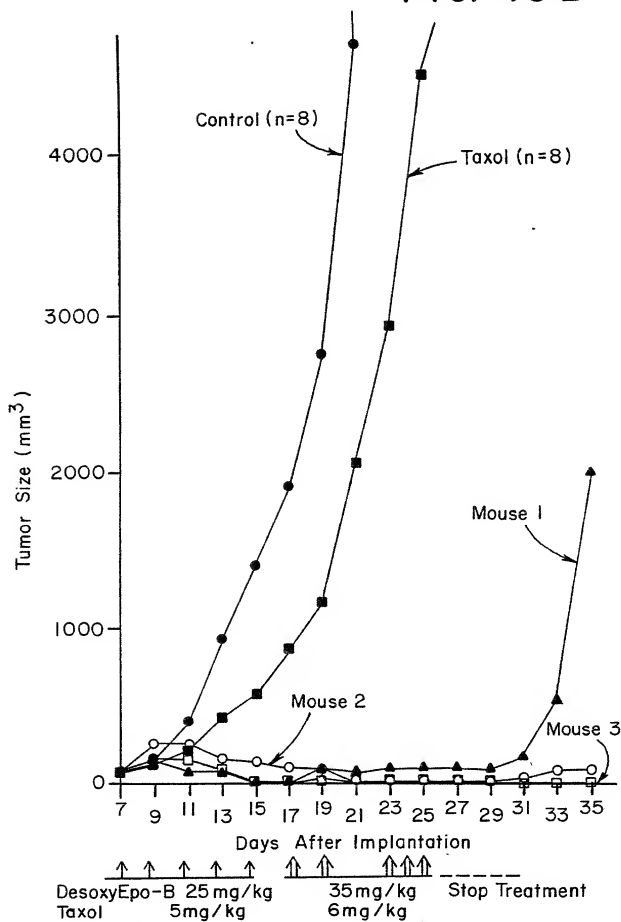
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FIG. 45A



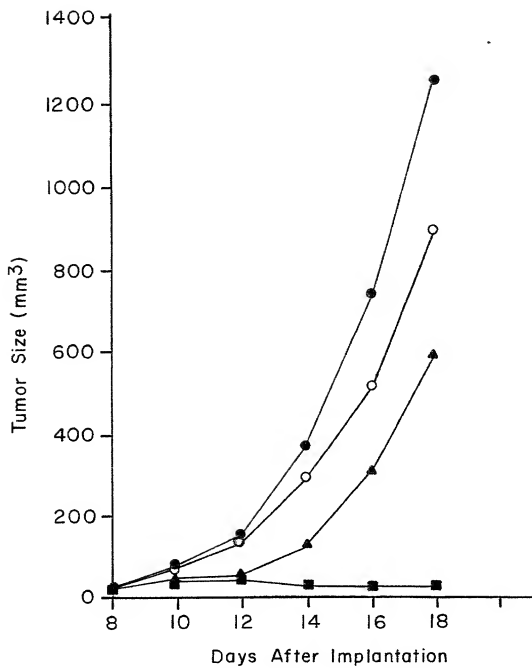
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FIG. 45B



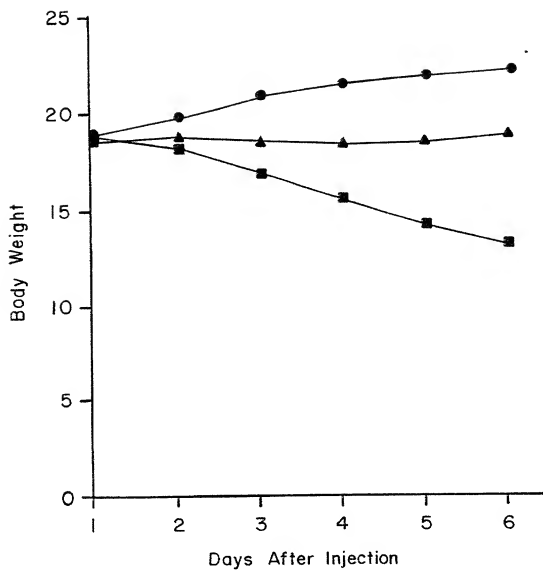
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FIG. 46



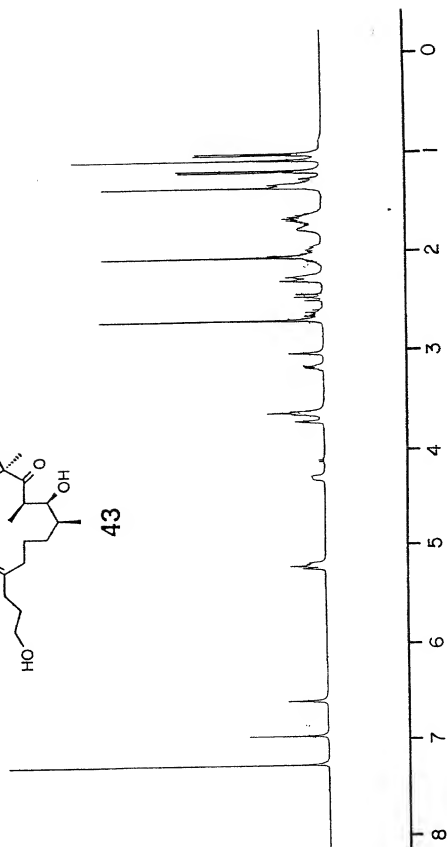
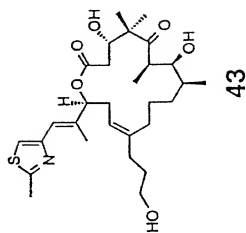
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FIG. 47



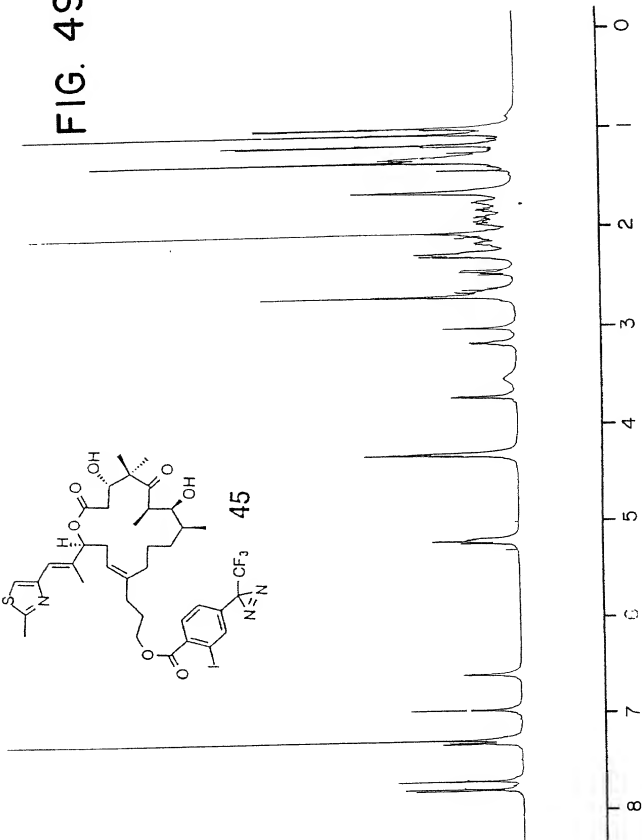
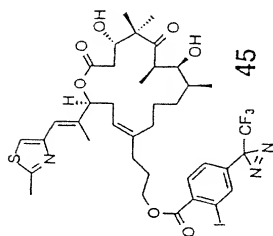
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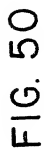
FIG. 48

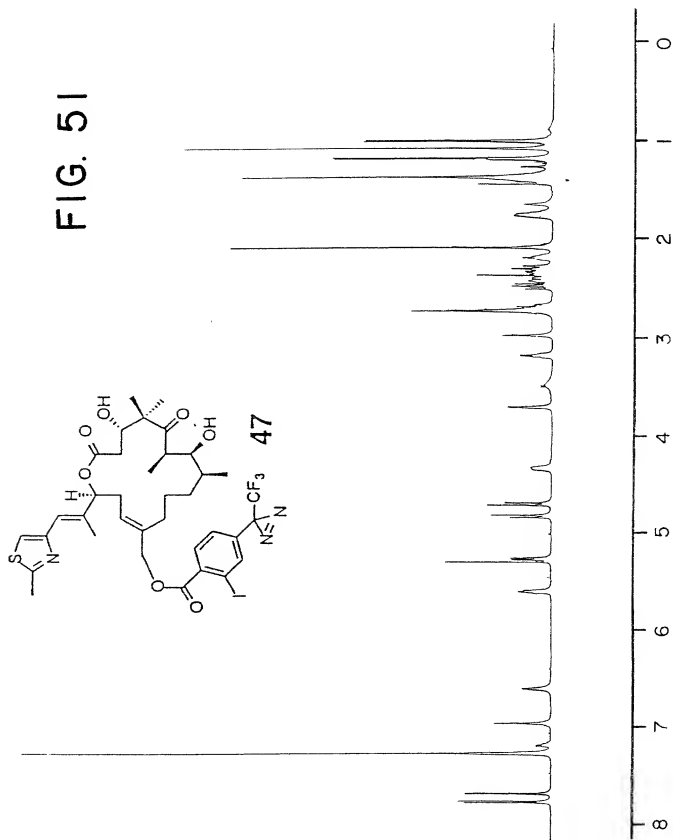


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FIG. 49







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FIG. 52

